chem 5390

Advanced X-ray Analysis

LECTURE 14

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Diffraction Theory

Phase Analysis - Vegard's Law

Good for alloys with continuous solid solutions

$$d_{hkl} = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

Ex) Au-Pd

- **To create the plot on the right**
  - **Using the crystal structure of the alloy calculate "a" for each metal**
  - **Draw a straight line between them as shown on the chart to the left.**
- **To calculate the composition**
  - **Calculate "a" from d-spacings**
  - **"a" will be an atomic weighted fraction of "a" of the two metal**

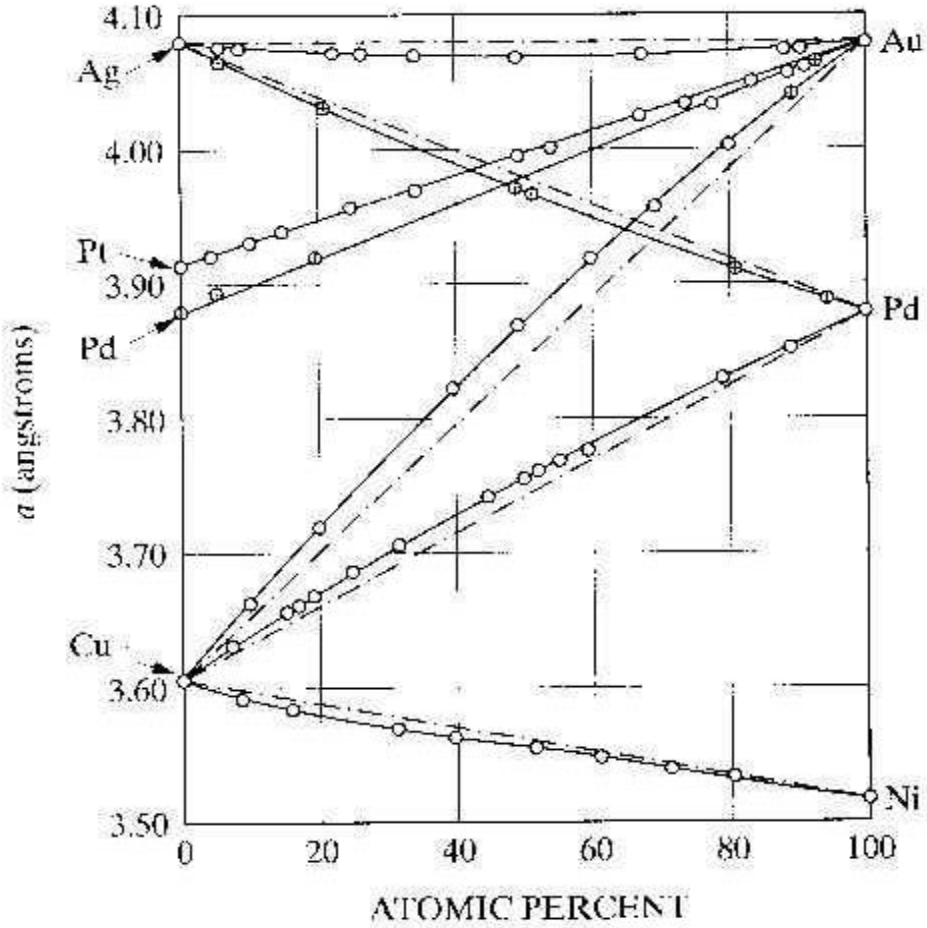


Figure 11-6 Lattice parameters of some continuous solid solutions. Dot-dash lines indicate Vegard's law. Barrett [1.7].

Diffraction Theory

Measuring Changes In Phase Fraction

Using I/Icor

$$\frac{I_{\alpha-\exp}(hkl)}{I_{\beta-\exp}(HKL)} = \frac{I_{\alpha}(hkl) \times {}^{I}\!/_{Icor\,\beta}(hkl) \times w_{\beta}}{{}^{I}\!/_{Icor\,\alpha}(hkl) \times I_{\beta}(hkl) \times w_{\alpha}}$$

– Where

- $\frac{I}{I_{cor}} = \frac{\text{Intensity of sample's 100\% peak}}{\text{Intensity of Corundum's 100\% peak}}$
- ω= weight fraction
- I(hkl)=Reference's relative intensity
- I_{exp}(hkl)=Experimental integrated intensity

Diffraction Theory

Measuring Changes In Phase Fraction

Using Direct Comparison Method

$$\frac{I_{\alpha-\exp}(hkl)}{I_{\beta-\exp}(HKL)} = \frac{R_\alpha \times v_\alpha}{R_\beta \times v_\beta}$$

$$\mathbf{R} = \frac{1}{V}\left[\mathbf{pCL_P}\left[\mathbf{F_{hkl}}\right]^2\right]$$

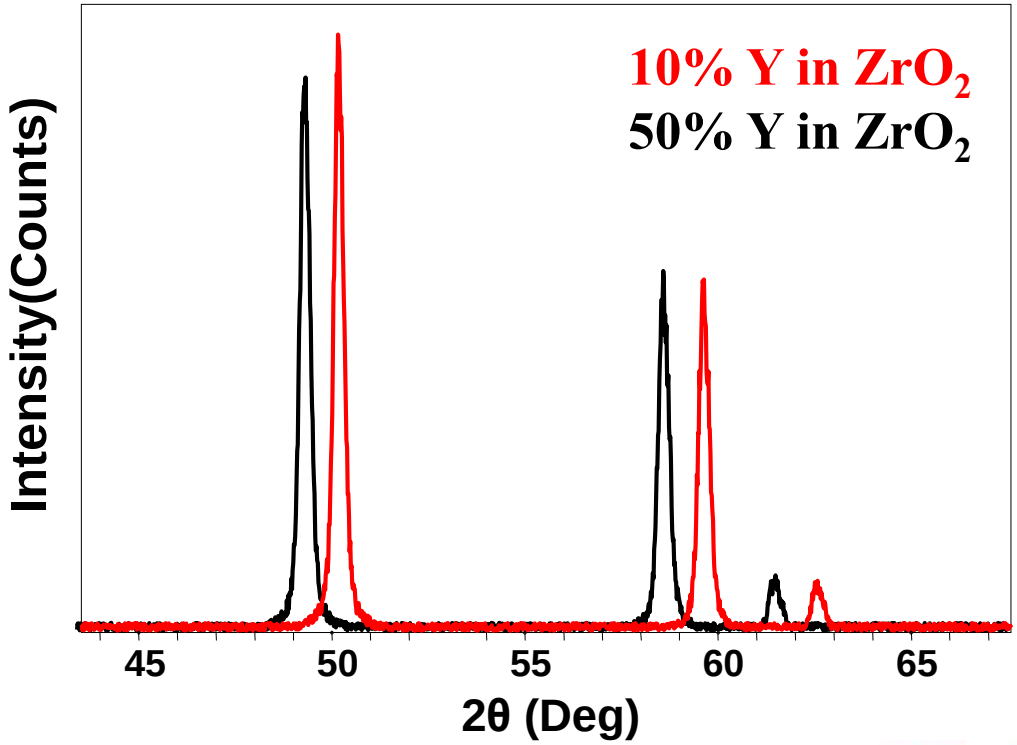
$$\mathbf{I_{hkl} = I_0 pCL_P}\left[\mathbf{F_{hkl}}\right]^2$$

Because this is already a complicated method, many choose to go ahead and use Rietveld Refinement

Diffraction Theory

Measuring Changes In Phase Fraction

Remember – changes in something like doping a sample can lead to changes in lattice parameters instead.



$R(Y^{3+}) = 0.104Å$

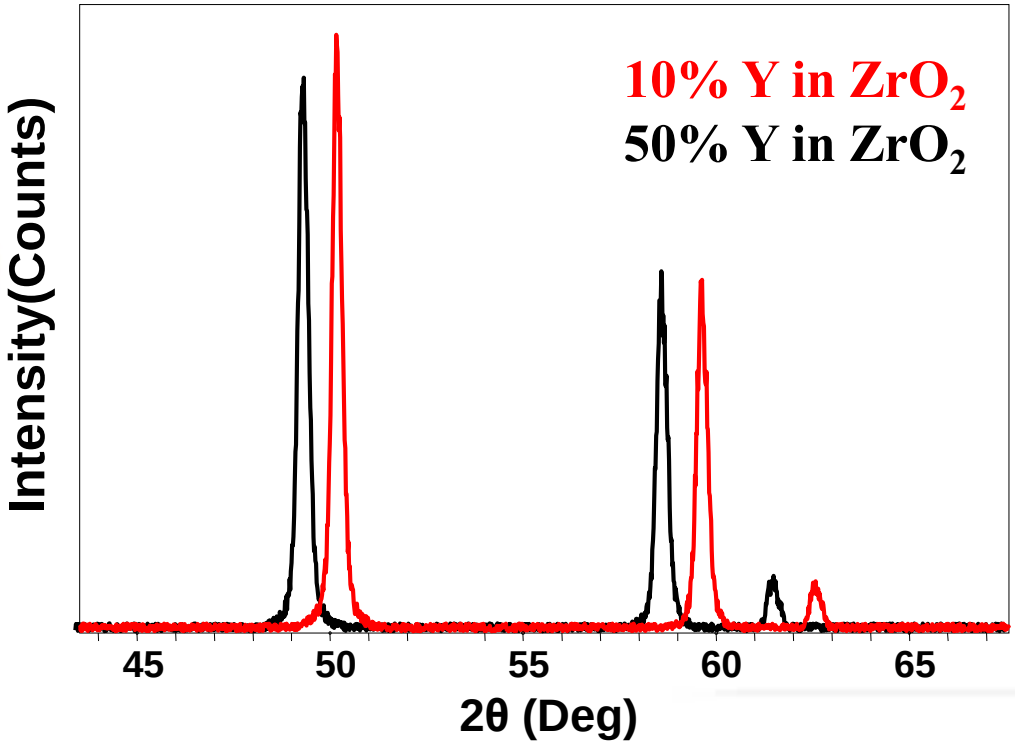
$R(Zr^{4+}) = 0.079Å$

Diffraction Theory

Measuring Changes In Phase Fraction

Substitutional doping can change bond distances, reflected by a change in unit cell lattice parameters

The change in peak intensity due to substitution of atoms with similar Z is much more subtle and may be insignificant



$R(Y^{3+}) = 0.104Å$

$R(Zr^{4+}) = 0.079Å$

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Diffraction Theory

Texture

Inducing texture in powder samples - causes peak intensities to vary

Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation

The measured diffraction pattern will not agree with that expected from an ideal powder

Diffraction Theory

Texture in samples is a common occurrence, and usually have more to do with how the samples are made.

-Plastically deformed metals (cold rolled, etc)

-Powders with particle shapes related to their crystal structure, particular planes form the faces

-Orientation in particular directions (Plates, needles, acicular, cubes, etc.)

Diffraction Theory

Orientation in particular directions (Plates, needles, acicular, cubes, etc.)

-Fiber Texture

A particular direction [uvw] for all grains is more or less parallel to the wire or fiber axis

e.g. [111] fiber texture in Al cold drawn wire

Double axis is also possible

Example: [111] and [100] fiber textures in Cu wire

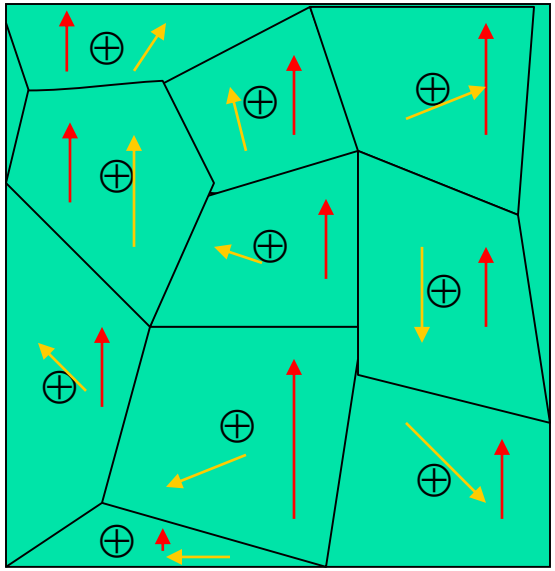
-Sheet Texture

Most of the grains are oriented with a certain crystallographic plane (hkl) roughly parallel to the sheet surface and certain direction [uvw] parallel to the rolling direction

Notation: (hkl)[uvw]

Diffraction Theory

Orientation in particular directions (Plates, needles, acicular, cubes, etc.)



Also, if the direction $[u_1v_1w_1]$ is parallel for all regions, the structure is like a single crystal

However, the direction $[u_1v_1w_1]$ is not aligned for all regions, the structure is like a mosaic structure, also called as **Mosaic Texture**

⊕ [uvw] i.e. perpendicular to the surface of all grains is parallel to a direction [uvw]

Diffraction Theory

Simple Means of Quantifying Texture

Lotgering degree of orientation (*f*)

- **A comparison of the relative intensities of a particular family of (hkl) reflections to all observed reflections in a coupled 2θ powder x-ray diffraction (XRD) Spectrum**
- ***f* is specifically considered a measure of the "degree of orientation" and ranges from 0% to 100%**
- **po is p of a sample with a random crystallographic orientation.**

$$f = \frac{p - p_o}{1 - p_o};$$

$$p = \frac{\sum I_{00l}}{\sum I_{00l} + \sum I_{non-00l}}$$

Diffraction Theory

Relative Texture Coefficient (RTC)

Relative peak intensities are analyzed by determining relative texture coefficients of the reflections present in the XRD pattern.

$$RTC_{hkl} = \frac{I_{p,hkl} / I^{\circ}_{p,hkl}}{\Sigma\, I_{p,hkl} / I^{\circ}_{p,hkl}} * 100\%$$

where $I_{p,hkl}$ is the intensity of the peak for each sample at each (hkl) reflection used.

$I^{\circ}_{p,hkl}$ is the intensity of those reflections for the standard reference (PDF# 00-000-0000) in the database.

The standard provides a random orientation pattern to compare against any preferred orientation found in the samples.

Diffraction Theory

Relative Texture Coefficient (RTC) Example: Golden et.al.

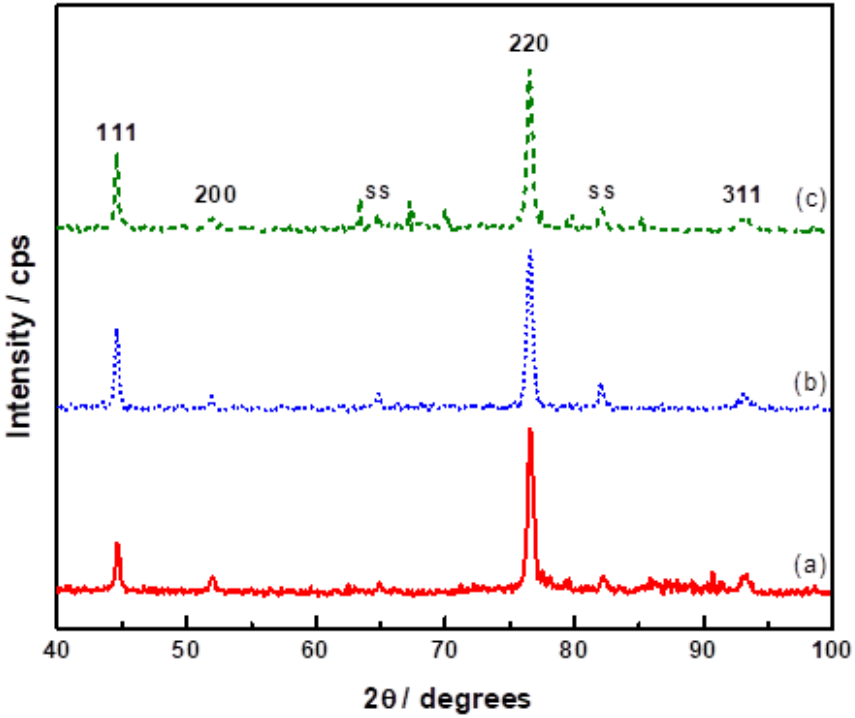


Table 2: Relative texture coefficients for (111), (200), (220), and (311) growth planes for each sample as measured with XRD.

Sample	RTC_{111}	RTC_{200}	RTC_{220}	RTC_{311}
A1	5.26	4.85	72.32	17.66
B1	8.09	4.32	71.84	15.74
B2	7.80	4.27	72.66	15.26

Diffraction Theory

Relative Texture Coefficient (RTC) Example: Golden et.al.

Figure S10. X-ray diffraction (XRD) of (a) pure Ni, (b) Ni CeO_2, and (c) Ni Fc-CeO_2 coatings

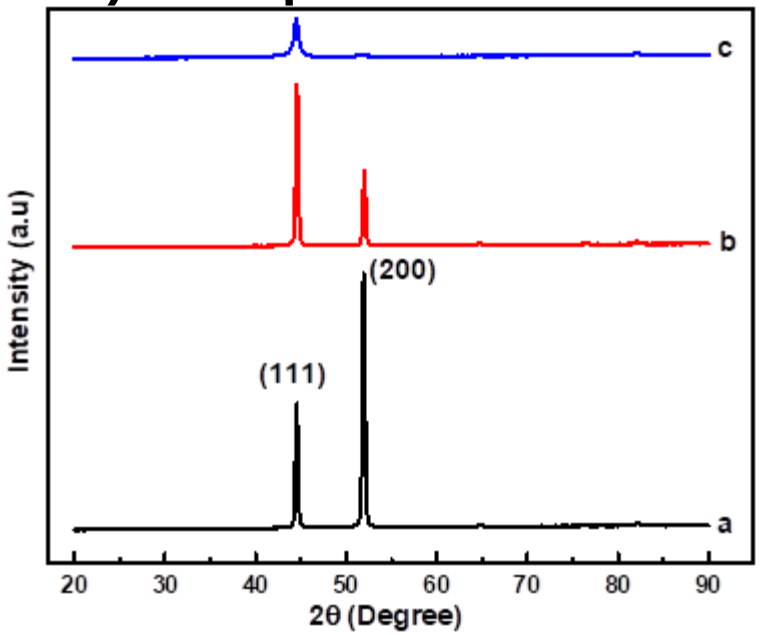
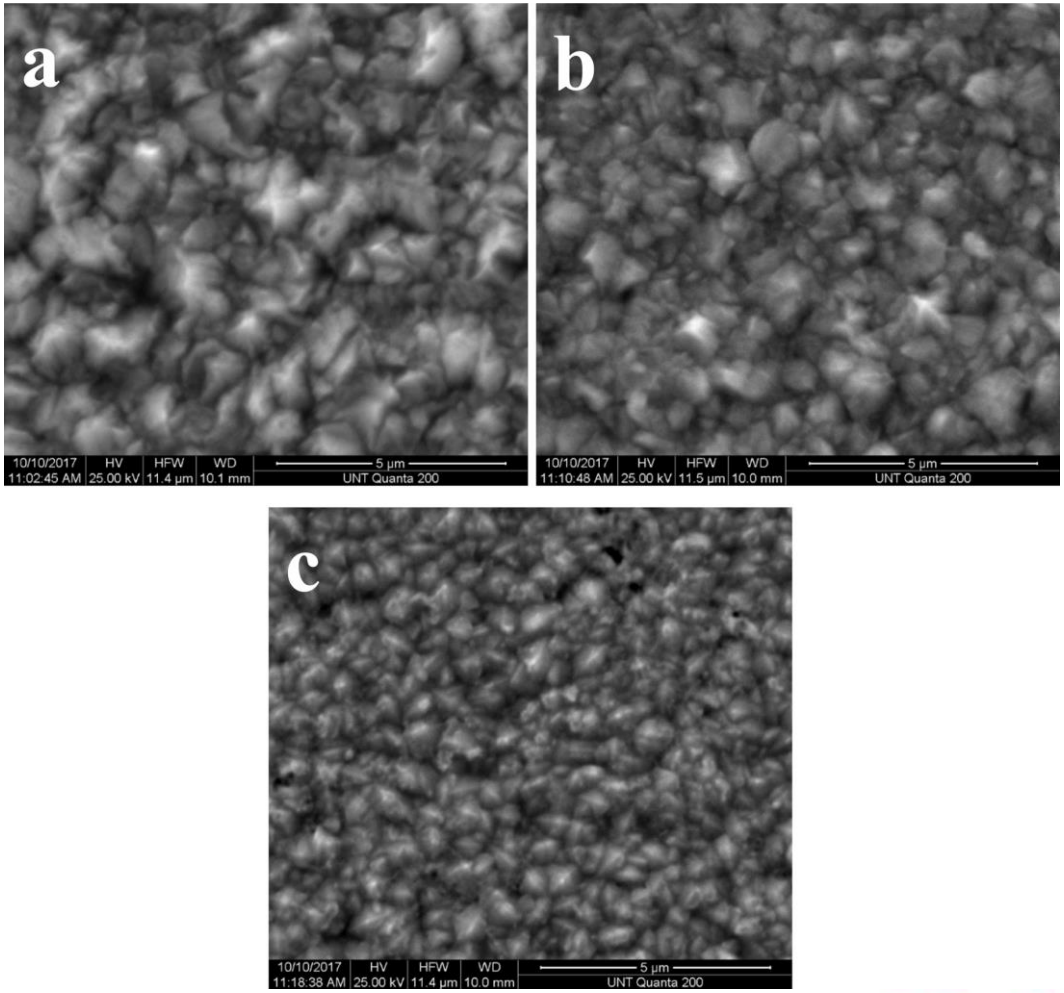


Table 2. XRD reflection intensities, relative texture coefficients, and crystallite sizes for Nickel, Ni CeO_2 and Ni Fc-CeO_2 electrodeposited coatings.

Coating (n=3)	$I(f)_{111}$	$I(f)_{200}$	$I(f)_{220}$	RTC_{111}	RTC_{200}	RTC_{220}	Crystallite size (nm)
PDF# 00-004-0850	100	42	21	---	---	---	---
Nickel	49	100	3	29.8	63.3	6.9	47.6 ± 5.0
Ni CeO_2	100	51	4	50.7	41.9	6.7	43.3 ± 6.3
Ni Fc-CeO_2	100	11	16	63.1	14.6	22.3	32.0 ± 5.5

Diffraction Theory

Relative Texture Coefficient (RTC) Example: Golden et.al.



Diffraction Theory

Pole Figure Analysis

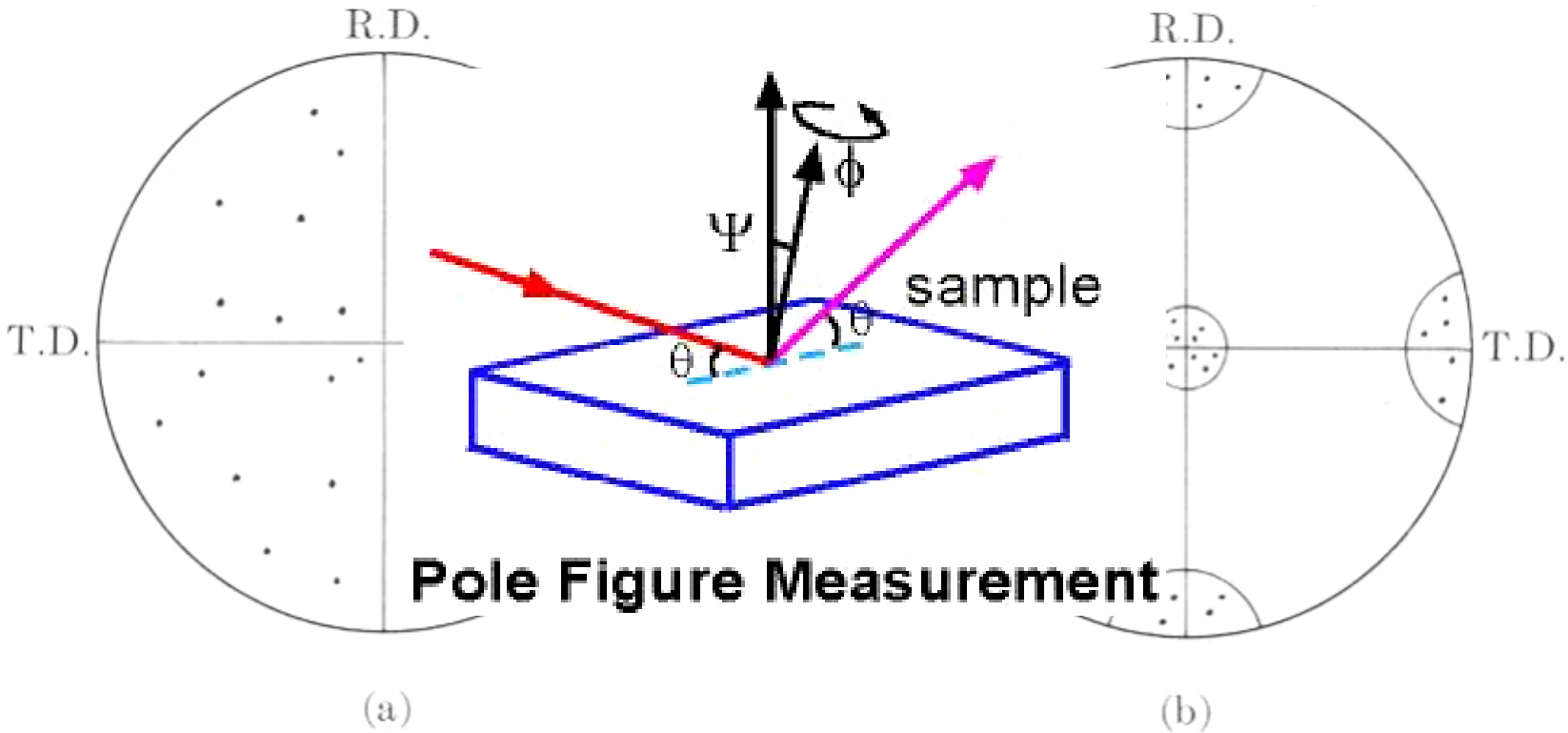
Texture Analysis Experiment

Measurement of texture (the non-random or preferred orientation of crystallites) involves measurement of the variations in intensity of a single Bragg reflection as the sample is both tilted (psi) and rotated (phi).

The result is plotted as a 'pole figure', in which the contours indicate intensity levels as a function of sample orientation.

Diffraction Theory

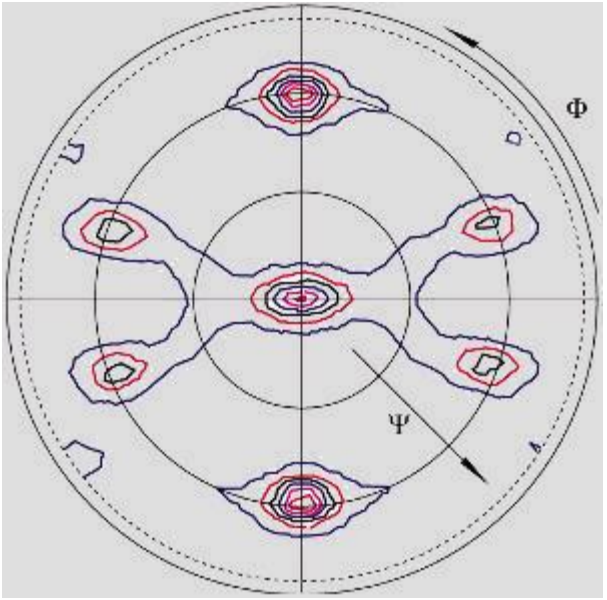
Texture Analysis



(100) pole figures for a sheet material
(a) Random orientation (b) Preferred orientation

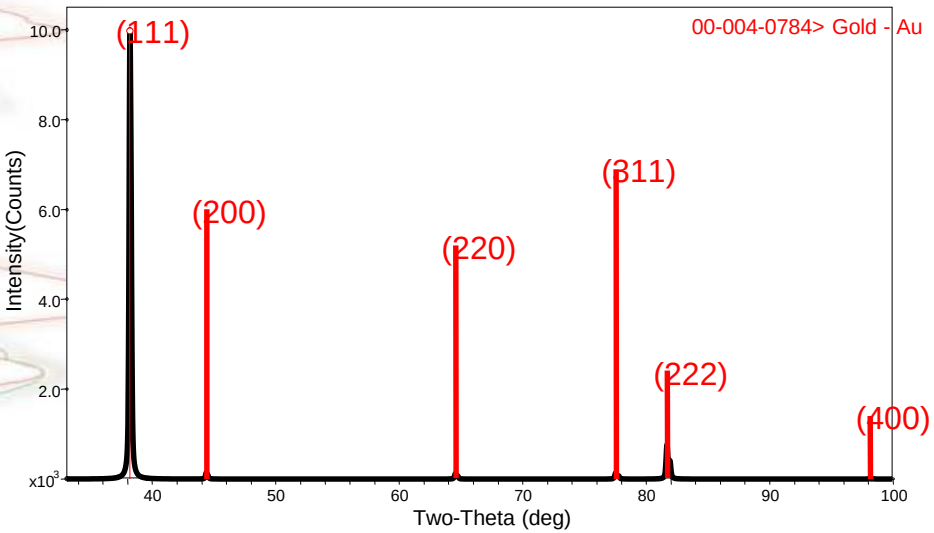
Diffraction Theory

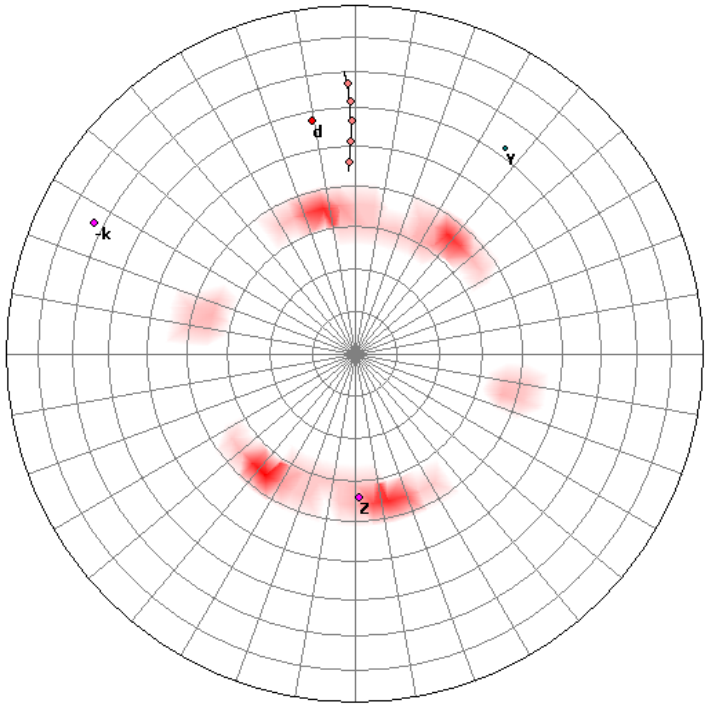
Texture Analysis



Diffraction Theory

Texture Analysis

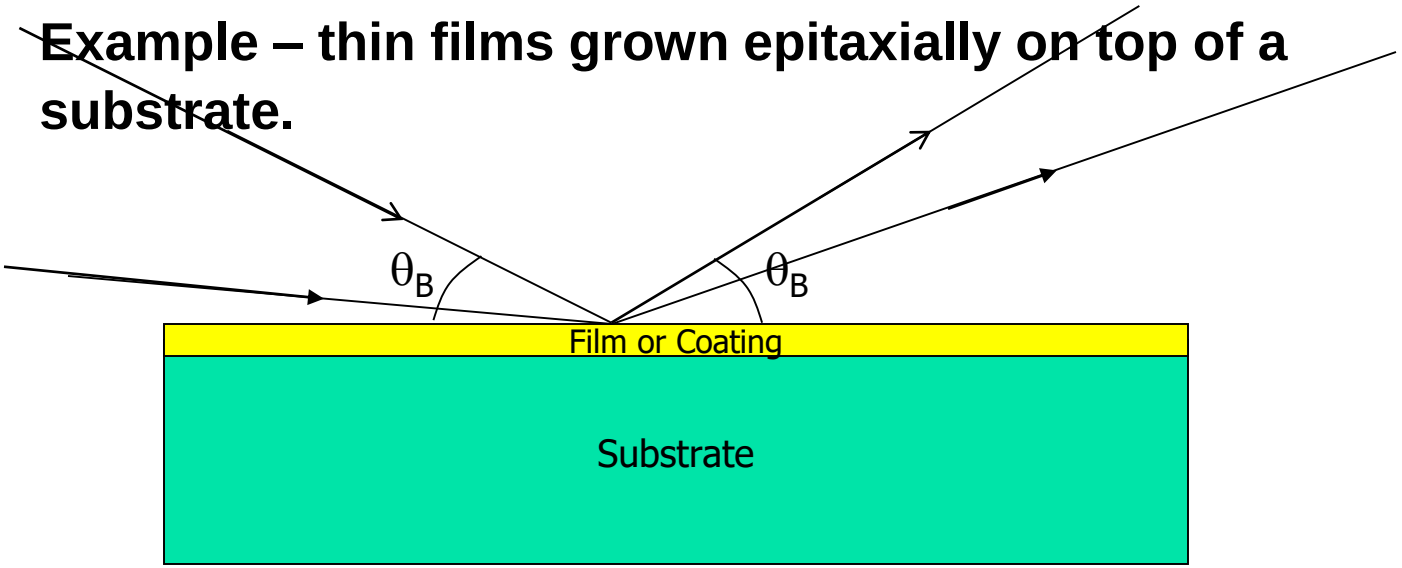




Diffraction Theory

Pole Figure Analysis

Example – thin films grown epitaxially on top of a substrate.



Diffraction Theory

Pole Figure Analysis

Epitaxial Films

An epitaxial film is a lattice-matched thin film grown on usually a single crystal substrate

– The lattice of the film is nearly identical to the lattice of the substrate

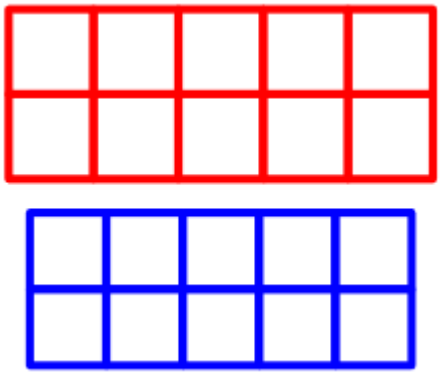
– When the film grows, its lattice changes (strains) in order to match the lattice of the substrate

– The atomic bonding across the substrate and film is "perfectly" matched

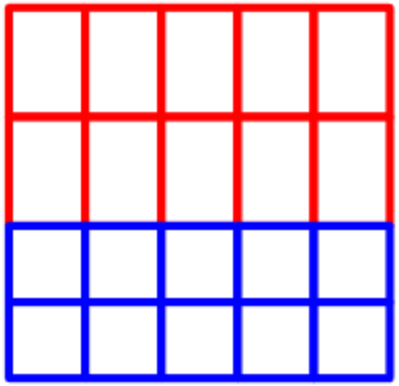
Diffraction Theory

Epitaxial Films

An epitaxial film is a lattice-matched thin film grown on usually a single crystal substrate



The lattice of the film (red) is almost the same as the substrate (blue)



The lattice of the epitaxial film (red) distorts to minimize the strain energy where it bonds to the substrate (blue)

Diffraction Theory

Texture Analysis

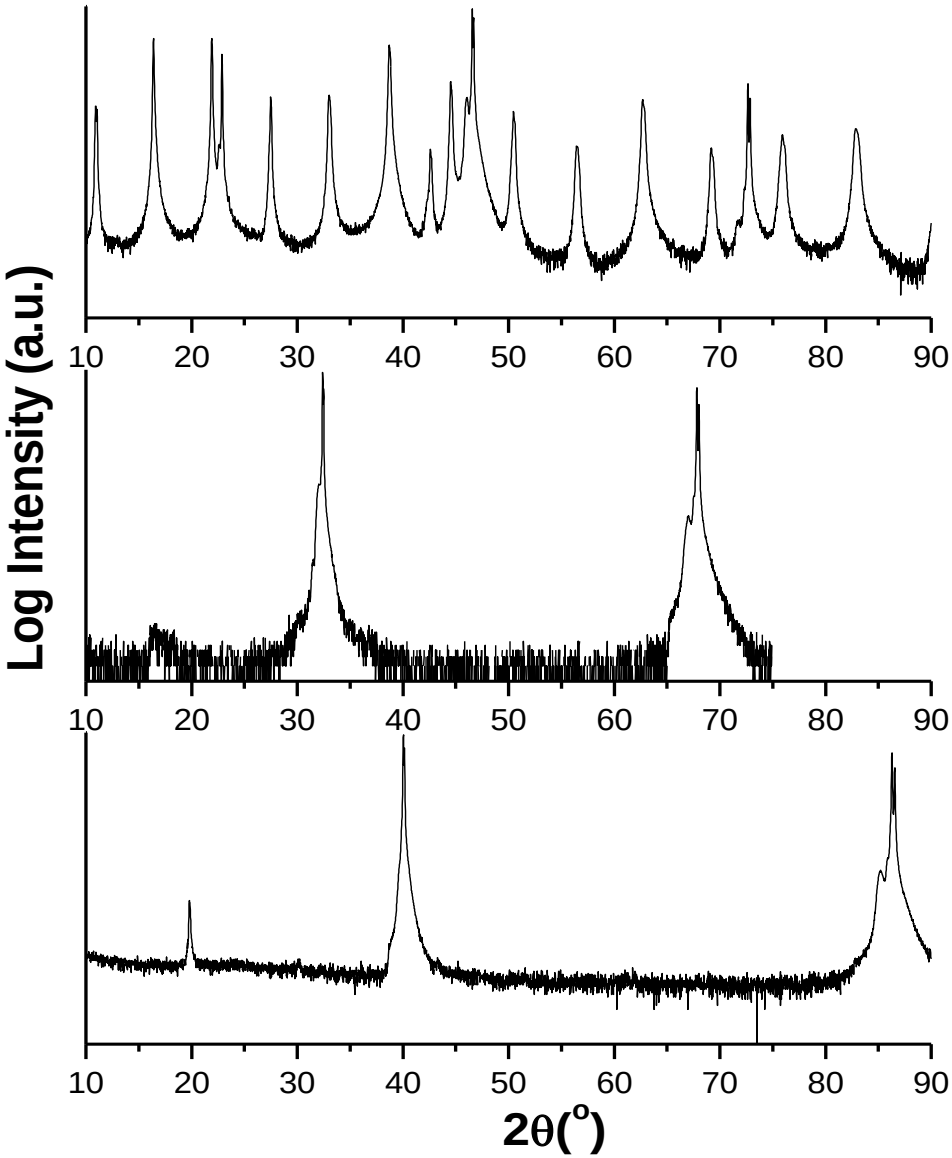
Example:

Bismuth Titanate thin films on oriented $SrTiO_3$ substrates

Only one type of peaks

It apparent that films are highly oriented

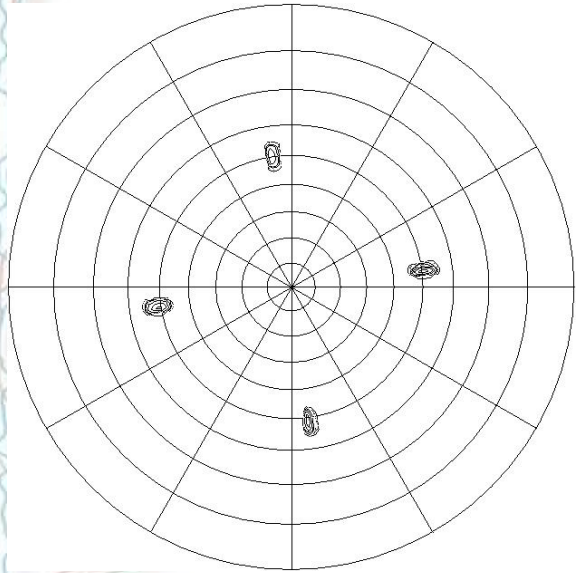
3 different examples



Diffraction Theory

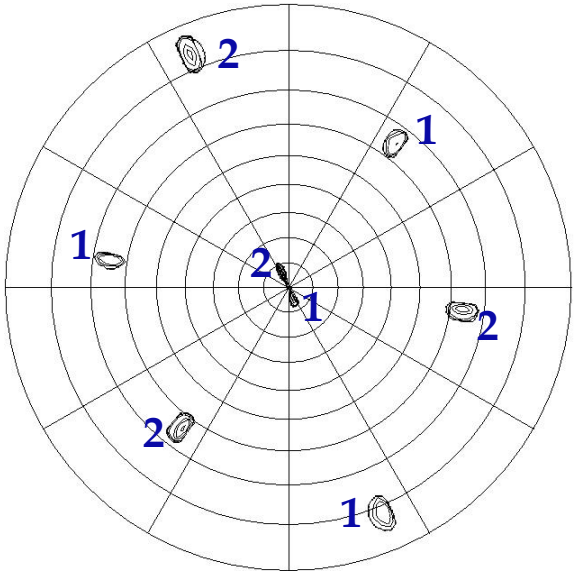
Pole Figure Analysis

$SrTiO_3$ (100)



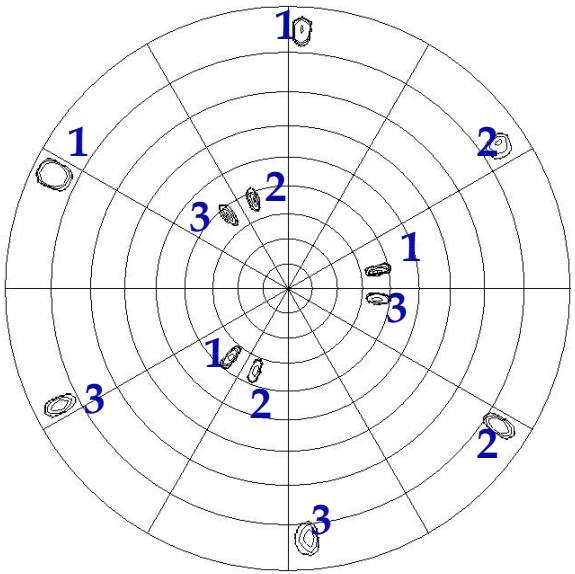
- 4 Peaks at ~50°
- Excellent in-plane orientation

$SrTiO_3$ (110)



- 2 sets of peaks at ~ 5, 65 and 85°
- Indicating a doublet or opposite twin growth

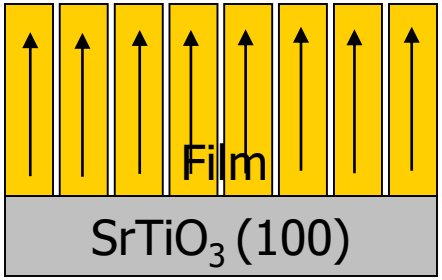
$SrTiO_3$ (111)

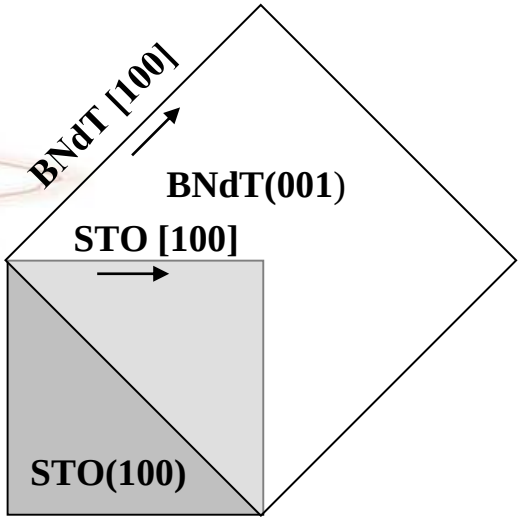


- 3 sets of peaks at ~ 35 and 85°
- indicating a triplet or triple twin growth

Diffraction Theory

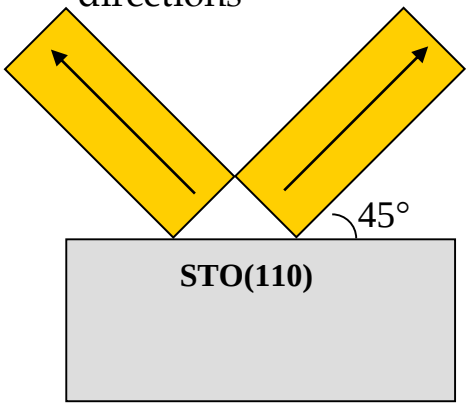
Texture Analysis Evolution





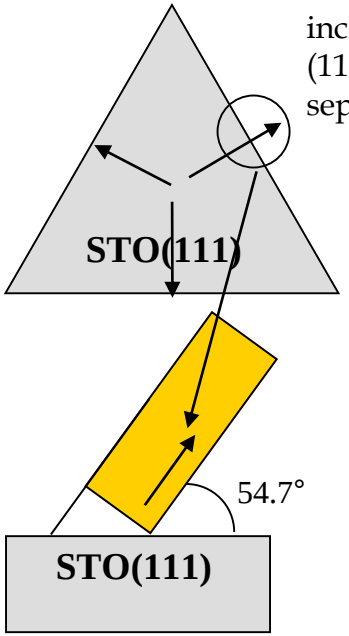
BNdT/SrTiO3 (100)

Two (100) planes inclined at 45° to (110) plane in opposite directions



BNdT/SrTiO$_3$ (110)

3 (100) planes inclined at 54.7° to (110) plane, separated by 120°



BNdT/SrTiO$_3$ (111)

Diffraction Theory

Rocking Curves

A useful method for evaluating the quality of oriented samples such as epitaxial films.

RC measurement reveals broadening of the diffraction peaks. The increase in the peak widths can be caused by:

-Mosaicity (misorientation of crystallites)

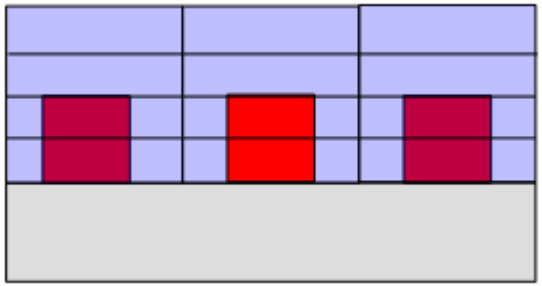
-Strain

-Limited layer thickness

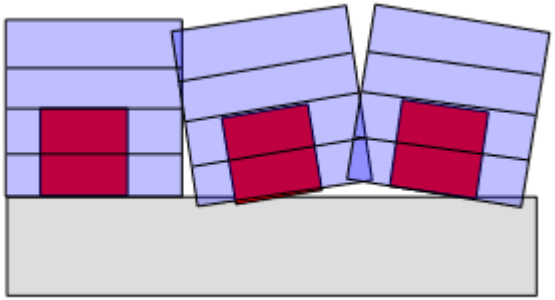
Diffraction Theory

Epitaxial Films – Mosaic Spread

Mosaicity is created by slight misorientations of different crystals as they nucleate and grow on the substrate. When the crystals join, they form low energy domain boundaries.



Ideal case, each nuclei (red) is perfectly oriented. When the crystals grow and meet, there is perfect bounding between the crystallites and therefore there is no grain boundary



If the nuclei (red) are slightly misaligned, then low angle domain boundaries will be formed.

Diffraction Theory

Rocking Curves

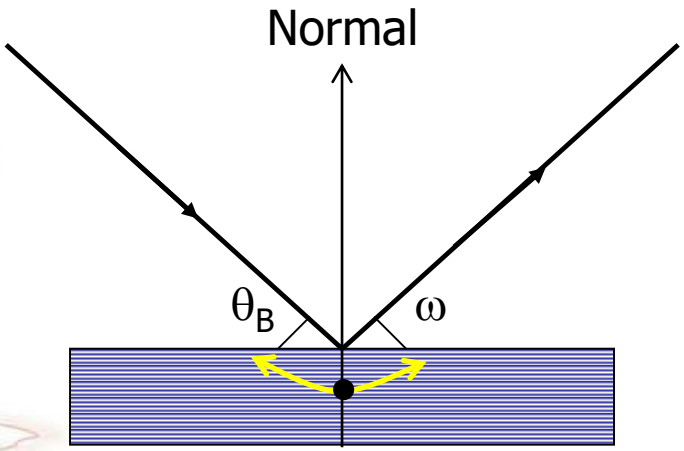
Typically XRD peak width is quantitatively described by Full-Width-at Half-Maximum (FWHM).

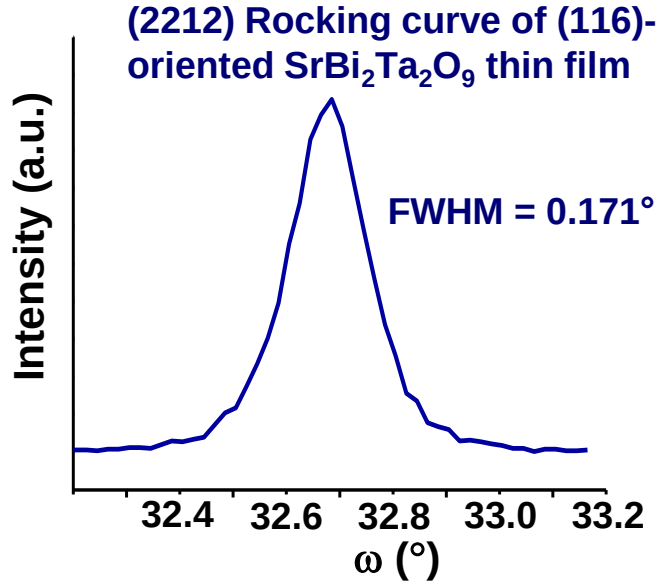
ω is changed by rocking the sample but θ_B is held constant

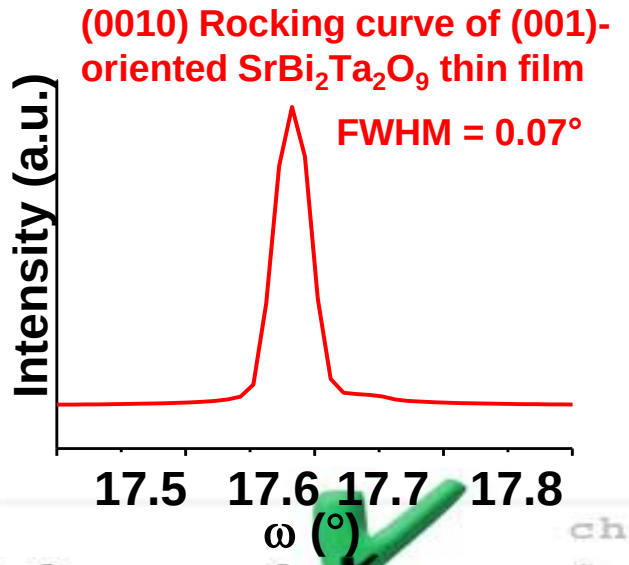
Width of Rocking curve is a direct measure of the range of orientation present in the irradiated area of the crystal

Diffraction Theory

Rocking Curves







Diffraction Theory

Summary

Perfect Epitaxy	Single crystal film in perfect registry with a substrate. There are no defects in the film or the substrate.
Nearly perfect epitaxy	Single crystal film in nearly perfect registry with a substrate. Both film and substrate contain a low concentration of defects. Most defects are dislocations in the film.
Textured epitaxial*	Film consists of mosaic domains in nearly perfect registry with the substrate. All domain boundaries are very low angle/low energy. There is nearly perfect bonding across domain boundaries.
Strongly textured polycrystalline	Film consists of grains with nearly perfect preferential orientation of all principle axes. This orientation is often strongly correlated to the substrate. Misorientation parameter for texture is small.
Textured polycrystalline	Film consists of grains with a preferred orientation for 3 principle axes or only along 1 axis out-of-plane.
Polycrystalline	Film consists of randomly oriented grains.
Amorphous	Film does not have long-range crystalline order.

Diffraction Theory

Summary

	Thickness	Composition	Lattice Strain/ Relaxation	Defects	Orientation	Residual Stress	Crystallite Size
Perfect Epitaxy	XRR, HRXRD	HRXRD, RC	Assume 100%	Assume none	HRXRD	--	--
Nearly perfect epitaxy	XRR, HRXRD	HRXRD, RC	HRXRD	RC	HRXRD	--	--
Textured epitaxial*	XRR, HRXRD	HRXRD	HRXRD, IP-GIXD	RC	HRXRD	--	--
Strongly textured polycrystalline	XRR	XRPD, IP-GIXD	IP-GIXD	XRPD, IP-GIXD	IP-GIXD, PF	IP-GIXD	XRPD, IP-GIXD
Textured polycrystalline	XRR	XRPD, GIXD or IP-GIXD	--	XRPD, GIXD OR IP-GIXD	PF	Psi	XRPD, GIXD
Polycrystalline	XRR	XRPD, GIXD	--	XRPD, GIXD	PF	Psi	XRPD, GIXD
Amorphous	XRR	--	--	--	--	--	--

XRR- X-Ray Reflectivity
HRXRD- High Resolution XRD using coupled scan or RSM
RC- Rocking Curve
XRPD- Bragg-Brentano powder diffraction
GIXD- grazing incidence XRD
IP-GIXD- in-plane grazing incidence XRD
PF- pole figure
Psi- $\sin^2$psi using parellel beam

Lab 3 – Due today

Lab 4 – Due 11-23-21

Reading Assignment:

Read Chapter 8 from:

-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 13 from:

-Elements of X-ray Diffraction, 3rd edition, by Cullity and Stock